

Progress Report: NNG04GG13G History of Presolar Grains
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2/22/05

Below we summarize the results of our investigations into the history of presolar grains that were conducted from January, 2004 through January, 2005.

Papers on the History of Presolar Grains

This has been a very productive period in which much of the laboratory work conducted in the previous year and during this funding cycle were brought to completion. In the last year we have published or submitted for peer review 4 research papers, 4 review papers, and 11 abstracts in research areas supported under this grant. Brief synopses of the results of the research papers are presented below (items 1-4), followed by short summaries of the topics discussed in the review papers items (5-8). Several areas of research are of course being actively pursued, and the appended list of abstracts gives citations to this ongoing work.

1) In a paper submitted to the *Astrophysical Journal*, Bernatowicz *et al.* (1995) report the results of an investigation into the physical conditions in the mass outflows of asymptotic giant branch (AGB) carbon stars that are required for the formation of micron-sized presolar graphite grains, with and without previously formed internal crystals of titanium carbide (TiC). A lower mass limit of $1.1 M_{\odot}$ for stars capable of contributing presolar grains to the solar nebula is derived. This mass limit, in conjunction with a mass-luminosity relation for carbon stars, identifies the region of the HR diagram relevant to the production of presolar graphite. Detailed dynamical models of AGB outflows, along with constraints provided by kinetics and equilibrium thermodynamics, indicate that grain formation occurs at radii from 2.3 – 3.7 A.U. for AGB carbon stars in the $1.1 M_{\odot} - 5 M_{\odot}$ range. This analysis also yields time intervals available for graphite growth that are on the order of a few years. By considering the luminosity variations of carbon stars, we show that grains formed during minima in the luminosity are likely to be evaporated subsequently, while those formed at luminosity maxima will survive.

We calculate strict upper limits on grain sizes for graphite and TiC in spherically symmetric AGB outflows. Graphite grains can reach diameters in the observed micron size range ($1.2 \pm 0.6 \mu\text{m}$) only under ideal growth conditions (perfect sticking efficiency, no evaporation, no depletion of gas species contributing to grain growth), and then only in outflows from carbon stars with masses $\lesssim 2.5 M_{\odot}$. Even with the same ideal conditions, however, it is impossible to produce TiC grains of sufficient size—the calculated TiC diameters fall short of the observed (tens of nm) sizes for presolar TiC by about an order of magnitude. In general, the mass loss rates that would be required to produce the observed grain sizes are at least an order of magnitude larger than observed maximum AGB carbon star mass loss rates. These results, as well as pressure constraints derived from equilibrium thermodynamics, force us to conclude that presolar graphite and TiC must form in regions of enhanced density (clumps, jets) in AGB outflows having small angular scales.

2) In a companion paper to the Bernatowicz *et al.* theoretical efforts described in (1), Croat *et al.* (2005) describe correlated TEM and NanoSIMS investigations of the same presolar graphites spherules from the Murchison meteorite, linking the isotopic anomalies with the mineralogy and chemical composition of the graphite and its internal grains. Refractory carbide grains (especially titanium carbide) are commonly found within the graphite spherules, and most have significant concentrations of Zr, Mo, and Ru in solid solution, elements primarily produced by s-process nucleosynthesis. The effect of chemical fractionation on the Mo/Ti ratio in these carbides is limited, and therefore from this ratio one can infer the degree of s-process enrichment in the gas from which the graphite condensed. The resulting s-process enrichments within carbides are large ($\sim 200\times$ solar on average), showing that most of the carbide-containing graphites formed in the mass outflows of asymptotic giant branch (AGB) stars. NanoSIMS measurements of these graphites also show isotopically light carbon (mostly in the $100 < ^{12}\text{C}/^{13}\text{C}$

< 400 range). The enrichment of these presolar graphites in both s-process elements and ^{12}C considerably exceeds that astronomically observed around carbon stars. However, a natural correlation exists between ^{12}C and s-process elements, as both form in the He intershell region of thermally-pulsing AGB stars and are dredged-up together to the surface. Their observation together suggests that these graphites may have formed in chemically and isotopically inhomogeneous regions around AGB stars, such as high density knots or jets. As shown in the companion paper, a gas density exceeding that expected for smooth mass outflows is required for graphite of the observed size to condense at all in circumstellar environments, and the spatially inhomogeneous, high-density regions from which they condense may also be incompletely mixed with the surrounding gas.

We have also greatly expanded the available dataset of presolar graphites ($N = 847$) and characterized them by their morphology (e.g. onion-type and cauliflower-type). This effort has also revealed two new, rare presolar phases (iron carbide and metallic osmium) that are now known to condense in circumstellar environments. Due to the peculiar gas composition needed to form these rare presolar grain types, the graphites containing them are more likely to originate in supernova outflows.

3) Stadermann *et al.* (2005) reported on the first coordinated NanoSIMS/TEM study of presolar graphite spherules from supernovae. The Murchison low-density separate KE3 contains a large number of internal TiC crystals, that range in size from 15 to 500 nm. We have studied one such graphite grain in great detail by successive analyses with SEM, ims3f SIMS, TEM and NanoSIMS. Isotopic measurements of the 'bulk' particle in the ims3f indicate a supernova origin for this graphite spherule. The NanoSIMS measurements of C, N, O and Ti isotopes were performed directly on TEM ultramicrotome sections of the spherule, allowing correlated studies of the isotopic and mineralogical properties of the graphite grain and its internal crystals. We found isotopic gradients in $^{12}\text{C}/^{13}\text{C}$ and $^{16}\text{O}/^{18}\text{O}$ from the core of the graphite spherule to its perimeter, with the most anomalous compositions being present in the center. These gradients may be the result of isotopic exchange with isotopically normal material, either in the laboratory or during the particle's history. No similar isotopic gradients were found in the $^{16}\text{O}/^{17}\text{O}$ and $^{14}\text{N}/^{15}\text{N}$ ratios, which are normal within analytical uncertainty throughout the graphite spherule. Due to an unusually high O signal, internal TiC crystals were easily located during NanoSIMS imaging measurements. It was thus possible to determine isotopic compositions of several internal TiC grains independent of the surrounding graphite matrix. These TiC crystals are significantly more anomalous in their O isotopes than the graphite, with $^{16}\text{O}/^{18}\text{O}$ ratios ranging from 14 to 250 (compared to a terrestrial value of 499). Even the most centrally located TiC grains show significant variations in their O isotopic compositions from crystal to crystal. Measurement of the Ti isotopes in three TiC grains found no variations among them and no large differences between the compositions of the different crystals and the 'bulk' graphite spherule. However, the same three TiC crystals vary by a factor of 3 in their $^{16}\text{O}/^{18}\text{O}$ ratios. It is not clear in what form the O is associated with the TiC grains and whether it is cogenetic or the result of surface reactions on the TiC grains before they accreted onto the growing graphite spherule. The presence of ^{44}Ca from short-lived ^{44}Ti ($t_{1/2} = 60\text{y}$) in one of the TiC subgrains confirms the identification of this graphite spherule as a supernova condensate.

4) Nguyen and Zinner (2004) reported on the initial discovery of presolar silicates in meteorites. Nine presolar silicate grains from the carbonaceous chondrite Acfer 094 were found. Their anomalous oxygen isotopic compositions indicate formation in the atmospheres of evolved stars. Two grains were identified as pyroxene, two as olivine, one as a silicate GEMS (glass with embedded metal and sulfides), and one as an Al-rich silicate. One grain is enriched in ^{26}Mg , which is attributed to the radioactive decay of ^{26}Al and provides information about mixing processes in the parent star. This discovery opens new means for studying stellar processes and conditions in various solar system environments.

5) Tielens, Waters and Bernatowicz (2005) address a number of key questions relevant to stardust in meteorites. Astronomical observations and analysis of stardust isolated from meteorites have revealed a highly diverse interstellar and circumstellar grain inventory, including both amorphous materials and highly crystalline compounds (oxides, silicates and carbonaceous). This dust is highly processed during its sojourn from its birthsite (stellar outflows and supernova explosions) to its incorporation into protoplanetary systems. Of particular importance is processing by cosmic rays in the interstellar medium and by strong shocks due to supernova explosions. The latter leads to rapid destruction due to sputtering by impacting gas ions and shattering due to grain-grain collisions. In recent years, much progress has been made in understanding the origin and evolution of interstellar dust. This is largely driven by new infrared spectroscopic tools becoming available for astronomical studies and ever more elegant laboratory techniques allowing a deeper and deeper probing of stardust isolated from meteorites. We consider such questions as "What is the inventory of dust entering the Solar Nebula?", "What processes played a role in its formation and evolution in the ISM?", and "What is the evidence for processing in protoplanetary systems?"

6) Lodders and Amari (2005) wrote a review that provides an introduction to presolar grains – preserved stardust from the interstellar molecular cloud from which our solar system formed – found in primitive meteorites. We describe the search for the presolar components, the currently known presolar mineral populations, and the chemical and isotopic characteristics of the grains and dust-forming stars to identify the grains' most probable stellar sources.

7) Bernatowicz, Croat and Daulton (2005) describe how laboratory microanalyses of presolar grains give direct information on the physical and chemical properties of solid condensates that form in the mass outflows from stars. This information can be used, in conjunction with kinetic models and equilibrium thermodynamics, to draw inferences about condensation sequences, formation intervals, pressures and temperatures in circumstellar envelopes and in supernova ejecta. We review the results of detailed studies of graphite, silicon carbide and nanodiamonds found in primitive meteorites, and use these to illustrate how microanalytical investigations, together with astronomical observation and theoretical models, can be used to develop a more complete and accurate picture of the astronomical environments in which grains form.

8) Amari (2005) discusses how studies of presolar grains have yielded a wealth of information on nucleosynthesis in stars, mixing in stars and stellar ejecta, and the temporal variation of compositions of the Galaxy, becoming a new field of astronomy. Presolar grains identified to date include diamond, silicon carbide (SiC), graphite, silicon nitride (Si₃N₄), oxides, silicates, and refractory carbides in graphite and SiC.

PAPERS and ABSTRACTS

2004 papers:

Nguyen A. N. and Zinner E. (2004) Discovery of ancient silicate stardust in a meteorite. *Science* **303**, 1496-1499.

2004 abstracts:

Croat T. K., Stadermann F. J., Zinner E., and Bernatowicz T. J. (2004) Coordinated isotopic and TEM studies of presolar graphites from Murchison. *Lunar Planet. Sci.* **XXXV**, Abstract #1353.

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2005 papers:

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- Tielens A. G. G. M., Waters L. B. F. M., and Bernatowicz T. J. (2005) Origin and evolution of dust in circumstellar and interstellar environments. In *Chondrites and the Protoplanetary Disk* (ed. A. N. Krot, E. R. D. Scott, and B. Reipurth), submitted.

2005 abstracts:

- Bernatowicz T. J., Akande O. W., Croat T. K., and Cowsik R. (2005) Constraints on grain formation around carbon stars from laboratory studies of presolar graphite. *Lunar & Planet. Sci. XXXVI*, Abstract #1509.
- Croat T. K., Stadermann F. J., and Bernatowicz T. J. (2005) Internal grains within KFC graphites: Implications for their stellar source. *Lunar & Planet. Sci. XXXVI*, Abstract #1507.
- Jadhav M., Maruoka T., Amari S., and Zinner E. (2005) Finally: Presolar graphite grains identified in Orgueil. *Lunar & Planet. Sci. XXXVI*, Abstract #1976.
- Nguyen A. N., Zinner E., and Stroud R. M. (2005) Continued characterization of presolar silicate grains from the Acfer 094 carbonaceous chondrite. *Lunar & Planet. Sci. XXXVI*, Abstract #2196.
- Stroud R. M. and Bernatowicz T. J. (2005) Surface and internal structure of pristine presolar silicon carbide. *Lunar & Planet. Sci. XXXVI*, Abstract #2010.
- Zinner E., Amari S., Jennings C., Mertz A. F., Nguyen A. N., Nittler L. R., Hoppe P., Gallino R., and Lugaro M. (2005) Al and Ti isotopic ratios of presolar SiC grains of type Z. *Lunar & Planet. Sci. XXXVI*, Abstract #1691.